

MICROCALORIMETER EDS MEASUREMENTS OF CHEMICAL SHIFTS IN Fe COMPOUNDS

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We report measurements of chemical shifts in the Fe-L x-ray lines of different Fe compounds from x-ray emission spectra acquired using a microcalorimeter energy dispersive spectrometer (EDS). The observed changes in peak position and relative intensity of the Fe-L x-ray lines are in agreement with measurements obtained using a wavelength dispersive spectrometer (WDS), demonstrating the usefulness of microcalorimeter EDS for high-energy-resolution x-ray microanalysis.

Chemical shifts result from changes in electron binding energies with the chemical environment of atoms. In x-ray spectra, chemical shifts lead to changes in x-ray peak positions, relative peak intensities, and peak shapes. These chemical bonding effects can be significant (with x-ray peak shifts on the order of 1 eV), particularly for x-ray lines resulting from transitions involving valence electrons of light elements such as B and C.¹

Previously, chemical shifts in x-ray spectra have been measurable only using the high energy resolution of WDS. Recently, we have developed a microcalorimeter EDS^{2,3} with an instrument-response energy resolution of ~4 eV FWHM (real-time analog processing) over the energy range from 0 keV to ~2 keV. This energy resolution is comparable to that of a WDS and for the first time is sufficient to allow EDS chemical shift measurements.

In this work, x-ray spectra of flat, polished Fe compounds (Fe, FeO-OH, Fe₂O₃, Fe₃O₄, FeS, and FeS₂) were acquired using a microcalorimeter EDS mounted on a commercial scanning electron microscope (SEM) column. Two representative microcalorimeter EDS spectra (Fe and FeO-OH) are shown in Fig. 1. Heat pulses were injected into the microcalorimeter at regular intervals and recorded as part of each x-ray spectrum. The resulting heat pulse peak position was monitored to ensure constant detector gain for different spectra.

Close correspondence is observed between microcalorimeter EDS spectra and WDS spectra obtained on the same specimens under similar operating conditions, as shown in Fig. 2. From an analysis of the microcalorimeter EDS spectra, the Fe L $\alpha_{1,2}$ peak in the FeO-OH spectrum is shifted by $0.8 \text{ eV} \pm 0.1 \text{ eV}$ with respect to the Fe L $\alpha_{1,2}$ peak in the Fe spectrum. In addition, the uncorrected Fe L β /L $\alpha_{1,2}$ integrated intensity ratio increases from 0.24 ± 0.02 (Fe) to 0.49 ± 0.02 (FeO-OH) in agreement with the WDS measurements reported here and earlier WDS measurements.^{4,5}

While peak shape measurements are not routinely performed in WDS analysis due to the extreme time penalty imposed by scanning, the EDS operation of the microcalorimeter ensures that all peak shapes and integrated peak intensities are readily accessible. With further improvements in the energy resolution of microcalorimeter EDS, analysis using peak shapes and positions may become practical and provide straightforward determination of chemical bonding states.

References

1. J. E. Holliday, *J. Appl. Phys.*, 38 (1967) 4720.
2. D. A. Wollman et al., *J. Microscopy*, 188 (1997) 196.
3. J. M. Martinis et al., these proceedings.
4. D. W. Fisher, *J. Appl. Phys.*, 36 (1965) 2048.
5. D. G. W. Smith and R. K. O'Nions, *J. Phys. D*, 4 (1971) 147.
6. Contribution of the U.S. Government; not subject to copyright.

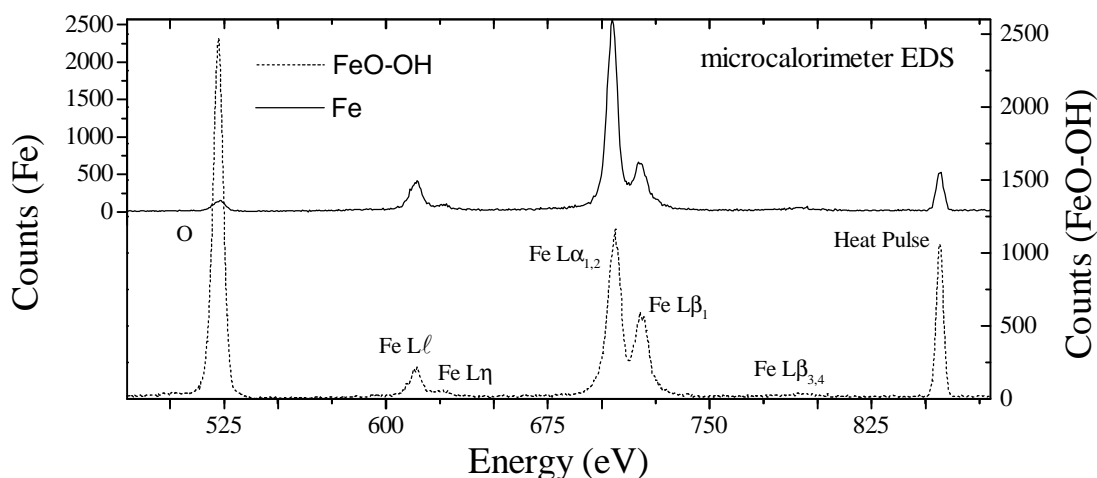


Fig. 1. Microcalorimeter EDS spectra of Fe (solid line) and FeO-OH (dashed line) acquired under the following conditions: 4096 channels, 5 keV beam voltage, 60 nA beam current, spot mode, live time 400 s, and an x-ray takeoff angle of 45°. The Fe spectrum was acquired with an input count rate of 340 s⁻¹, an output count rate of 250 s⁻¹, and a dead time of 26%, while the FeO-OH spectrum was acquired with an input count rate of 370 s⁻¹, an output count rate of 260 s⁻¹, and a dead time of 29%. The original Fe and FeO-OH spectra were identically corrected for energy nonlinearity, resulting in an approximately constant energy binwidth of 0.6 eV per channel over the energy range presented. The Fe spectrum includes a small O peak due to the presence of a native oxide; a significant C contamination peak was also observed for both spectra.

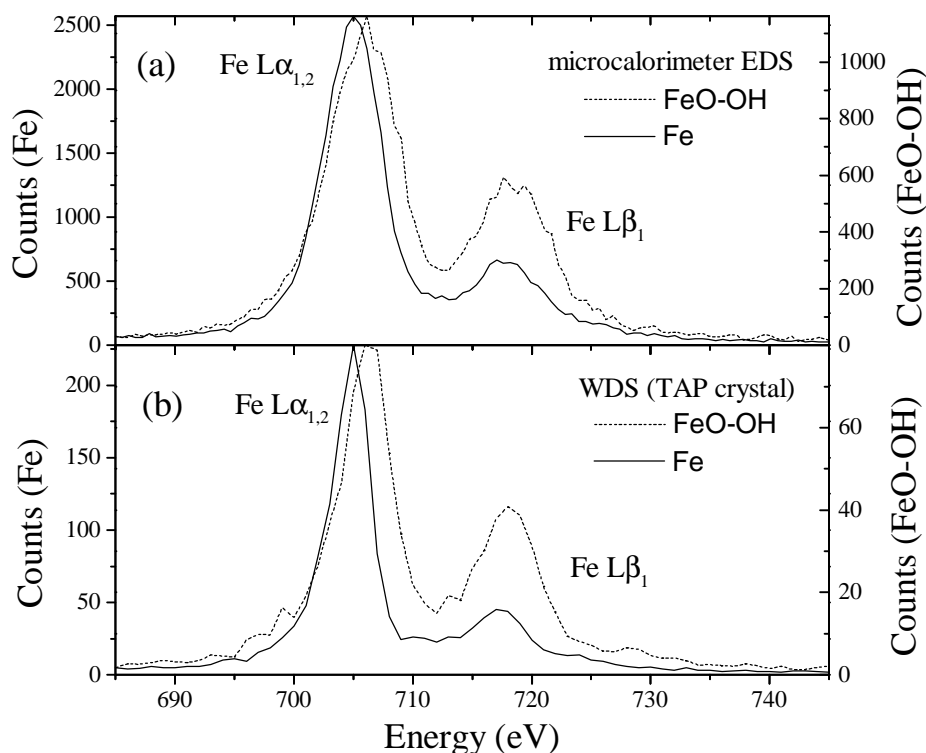


Fig. 2. (a) Expanded view of the Fe (solid line) and FeO-OH (dashed line) microcalorimeter EDS spectra shown in Fig. 1. (b) WDS spectrum of Fe (solid line) and FeO-OH (dashed line), acquired under the following conditions: 5 keV beam voltage, 50 nA beam current, thallium acid phthalate (TAP) crystal, 1 s per point, total time 100 s, and an x-ray takeoff angle of 40°. The WDS spectrum was converted to an EDS energy scale and rebinned using an energy binwidth of 1 eV per channel.